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Acrylonitrile Copolymerizations. II. Sequence Distribution in Methyl-Methacrylate Copolymers

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SUMMARY

The distributions of the sequences of methyl methacrylate units are calculated, first by taking into account and then ignoring the effects of the penultimate units on the reactivity of the growing radicals, previously deduced from kinetic measurements. The study of the infrared and NMR spectra of a set of copolymers covering the whole range of composition does support the occurrence of these penultimate effects. Admitting these effects, it is possible to propose the assignments of several bands in the methoxy and α -methyl regions of the NMR spectra.

INTRODUCTION

Kinetics studies carried out concerning the copolymerization of acrylonitrile (A) with either methyl methacrylate (M) or styrene [1, 2] have shown that the classical theory which associates each monomer with only one reactivity ratio is not valid for the whole range of composition of the monomer feed. The results obtained while studying the extreme ranges, where one of the monomers is present in small concentration, may be explained by assuming the effects of penultimate (or even antepenultimate) units on the reactivity of the growing radicals. However, these effects are not really proved, because the reactivity ratios of the different radicals are deduced from the fit of the experimental data with linear plots in coordinate systems that are chosen by assuming the occurrence of these penultimate effects. These plots are the linear representation of either the Barb equation [3] or simplified forms of the Alfrey [4] or Ham [5] equations. In a recent theoretical study of the penultimate effects, Berger and

Kuntz [6] have shown that the distributions of sequence lengths of the different units are more sensitive to the penultimate effects than the composition, which is generally used as a characterization of the copolymers; it follows that the proof of the penultimate effects is to be obtained from a study of these distributions.

A recent study of the A-M copolymers by Schmolke et al. [7], has shown that some results, unfortunately not precise or complete enough, may be obtained using IR spectroscopy. A preliminary study of the NMR spectra of some of these copolymers allowed us [8] to observe new resonance bands for the methoxy and α -methyl protons of the M units adjacent to A units. Such results suggested that we use IR and NMR techniques to precise the sequence distribution or at least some of its characteristics.

Our study includes, first, a theoretical study of the difference in the composition, the average sequence length, and the distribution of the sequences of different lengths, first taking into account and then ignoring the penultimate effects; then we shall present the results of our IR study, and the qualitative and quantitative studies of the NMR spectra, which support the actual occurrence of penultimate effects.

THEORETICAL STUDY

Berger and Kuntz [6] have reported that the composition of a copolymer is not sensitive to penultimate or remote-units effects. Their statement was supported by examples taken from the medium composition range. Such calculations are, of course, correct and Fig. 1 shows the very small discrepancy between the experimental

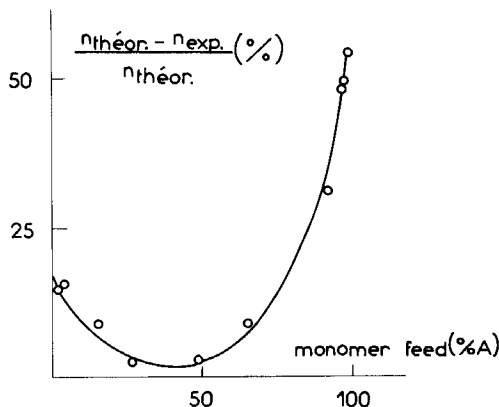


Fig. 1. Discrepancy between experimental and theoretical $n = dM/dA$ in the absence of penultimate effects.

compositions of the methyl methacrylate-acrylonitrile copolymers and the calculated ones using the observed values of the reactivity ratios $r_A = 0.25$ and $r_M = 1.20$ in the medium part of the composition range. However, the discrepancies are important in the extreme parts of the range, rising up to 50% and more.

The precise determination of the monomer consumptions, using gas chromatographic analysis, allowed us [2] to obtain the following data for the reactivity ratios, taking into account penultimate effects for each kind of polymer radical.

$$\begin{aligned} r_{AA} &= 0.39 & r_{MA} &= 0.20 \\ r_{MM} &= 1.01 & r_{AM} &= 1.56 \end{aligned}$$

From these values, we have calculated the number-average sequence length \bar{L}'_n for acrylonitrile or methyl methacrylate sequences, and also the distribution of the number or weight fractions W'_n and W'_w . These values were compared to the corresponding ones, \bar{L}_n , W_n , and W_w , obtained from the classical theory using only one reactivity ratio for each monomer. These expressions are as follows:

$$\bar{L}'_M n = \frac{\sum_1^{\infty} mn_M(m)}{\sum_1^{\infty} n_M(m)} = \frac{1}{P_{MA}} \quad (1)$$

and

$$\bar{L}'_M n = \frac{P_{MMA} + P_{AMM}}{P_{MMA}} \quad (1')$$

where $n_M(m)$ is the number of sequences of M units having the length m , P_{MA} is the probability of the addition of a A unit to an M-ended radical, P_{MMA} is the probability of the addition of a A unit to an MM-ended radical, and so on. These probabilities are related to the reactivity ratios and the composition of the feed as follows:

$$P_{MA} = \frac{1}{1 + r_M x_M} \quad P_{MMA} = \frac{1}{1 + r_{MM} x_M} \quad P_{AMM} = \frac{r_{AM} x_M}{1 + r_{AM} x_M}$$

where x_M is the molar ratio $x_M = M/A$. These expressions are plotted in the Fig. 2 as a function of the composition of the monomer feed.

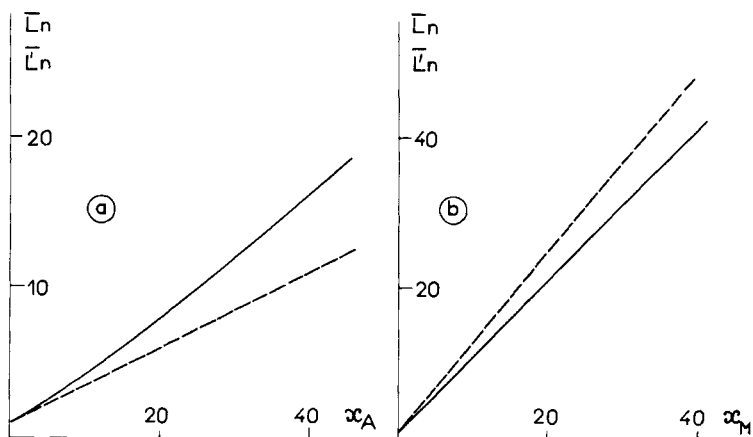


Fig. 2. Influence of penultimate effects on average number sequence length. a, A sequences; b, M sequences; —, with penultimate effects; — —, without penultimate effects. \bar{L}_n ; average number of M sequence lengths, with penultimate effects; \bar{L}'_n ; average number of M sequence lengths, without penultimate effects.

For the weight fractions the expressions are, for the number average,

$$W_M n(m) = \frac{n_M(m)}{\sum_1^{\infty} n_M(m)} = P_{MM}^{m-1} \cdot P_{MA} \quad (2)$$

and

$$W'_M n(m) = P_{AMM} \cdot P_{MMA} P_{MMM}^{m-2} \quad (2')$$

and for the weight average,

$$W_M w(m) = \frac{mn_M(m)}{\sum_1^{\infty} mn_M(m)} = m P_{MA}^2 P_{MM}^{m-1} \quad (3)$$

and

$$W'_{Mw}(m) = \frac{P_{MMA}^2 P_{AMM} P_{MMM}^{m-2}}{P_{MMA} + P_{AMM}} \quad (3')$$

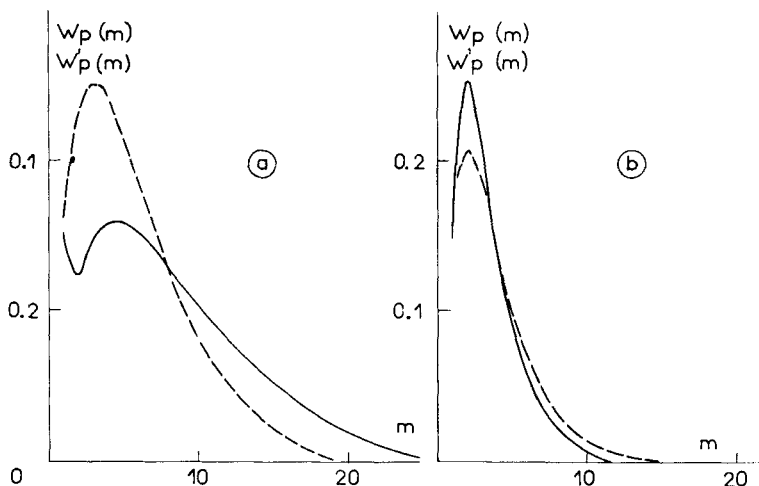


Fig. 3. Influence of penultimate effects on sequence distribution. a, A sequences for $X_A = A/M = 10.2$; b, M sequences for $X_M = M/A = 1.12$; —, with penultimate effects; ---, without penultimate effects; W_n , weight fraction of sequences of length m without penultimate effects; W'_n , weight fraction of sequences of length m with penultimate effects.

The corresponding plots are presented in Fig. 3.

The percent of M units included in a sequence of one, two, three units, and more, have been calculated as a function of copolymer composition. These calculations are illustrated in Figs. 4-7. It may be seen that, in agreement with the findings of Berger and Kuntz, the influence of the penultimate effects on the distribution of sequences length is the most pronounced for the short sequence in copolymers of medium composition. Such copolymers have been chosen for analytical study by IR and NMR spectroscopy. Their composition does not vary much during the conversion of the monomers, so that in most cases it was not necessary to use only low-conversion copolymers.

INFRARED SPECTROSCOPY

The measurements were performed with copolymer films cast from solutions in chloroform or acetone using Perkin-Elmer 125 and 225 apparatus.

According to Schmolke et al. [7] the 1060-cm^{-1} band was studied chiefly. This band is present in copolymers rather rich in M units

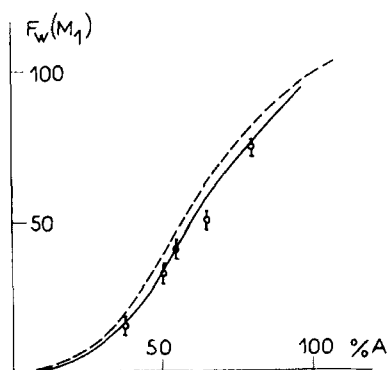


Fig. 4. Percentage of isolated M units (M_1). —, without penultimate effects; ---, with penultimate effects; $\bar{\phi}$, NMR determinations.

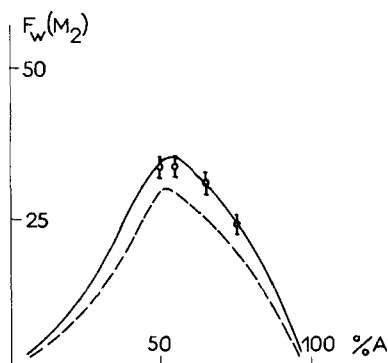


Fig. 5. Percentage of 2 M-unit sequences (M_2). ---, without penultimate effects; —, with penultimate effects, $\bar{\phi}$, NMR determinations.

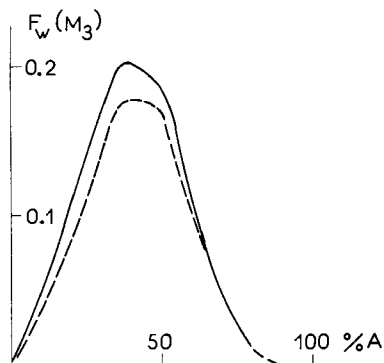


Fig. 6. Percentage of 3 M-unit sequences (M_3). —, with penultimate effects; ---, without penultimate effect.

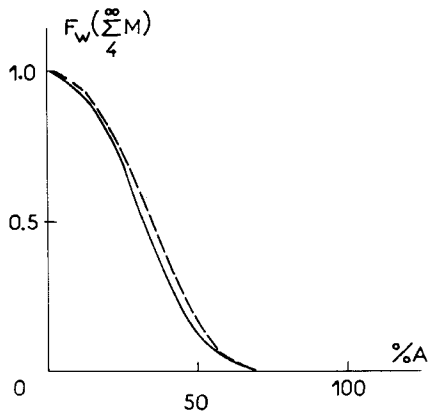


Fig. 7. Percentage of sequences of length greater than 3 M units. —, with penultimate effects; ---, without penultimate effects.

and is attributed to the vibrations of the α -CH₃ groups in syndiotactic configuration of the long M sequences (greater than 3 units). Its intensity (compared with the intensity of the 840-cm⁻¹ band characteristic of the M units also, but independent of the configuration) decreases when the percentage of A units in the copolymer increases, as a consequence of the shortening of the M sequences. Using the Schmolke assumption, the fraction of α -CH₃ groups in syndiotactic configuration was plotted in Fig. 8 versus the A con-

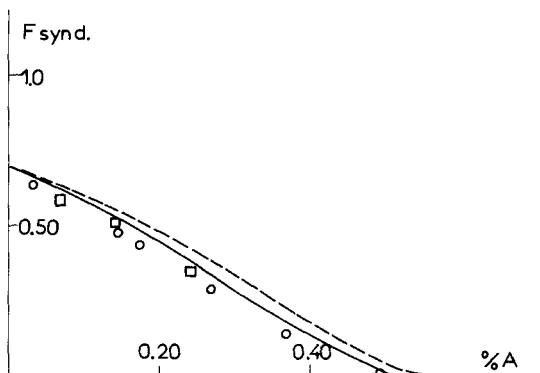


Fig. 8. Fraction of α -CH₃ in syndiotactic configuration versus copolymer composition (% A). —, with penultimate effects; ---, without penultimate effects; \circ , our data; \square , data from Schmolke and colleagues [7].

tent in the copolymers. Curve 1 corresponds to the calculation assuming that the M-sequences distribution is governed by Bernoullian statistics (no penultimate effect); using the first-order Markov assumption (simple penultimate effect) one obtains curve 2. The experimental points fit curve 2 more closely, but their position under this curve might indicate that remote unit effects are more important than the penultimate one. It is possible also that the 1060-cm⁻¹ band is to be associated with an M-units sequence of length greater than 3 units. This band actually disappears in a copolymer containing 50% A. For this copolymer, using the classical theory (no penultimate effects), it is found that 17% of M sequences are greater than 3 units, 7% greater than 4, and 2.5% greater than 5 units. The corresponding values taking into account the penultimate effects are 13, 4.5, and 1%, respectively. The discrepancy might be explained also assuming that, in statistics more complex than the Bernoullian ones, the percentage of syndiotactic configuration would be smaller.

NMR SPECTROSCOPY: QUALITATIVE STUDY

The measurements were carried out at 60 MHz with a Varian DA-60-IL spectrometer, using hexamethyldisiloxane (HMDS) as internal reference [$\tau(\text{HMDS}) = 9.95 \times 10^{-6}$]. The solvent was pyridine at 100°C for copolymers containing up to 60% A and aqueous pyridinium chloride for copolymers containing between 60 and 80% A.

In the NMR spectrum of poly(methyl methacrylate) (radical polymerization at 60°C), presented in Fig. 9, the singlet at 6.42 τ (a) is attributed to the methoxy protons and the three singlets at 8.65 τ (b), 8.77 τ (c), and 8.88 τ (d) are attributed to the α -methyl protons in isotactic, heterotactic, and syndiotactic triads, respectively. The bands corresponding to the β -CH₂ protons in isotactic diads are not well resolved, and the three domes centered at 7.86 τ , 7.92 τ , and 7.98 τ have been attributed to the β -CH₂ protons in hSh, hSs, and sSs syndiotactic tetrads [9].

In a previous study [8] we have shown that the presence of A units in the copolymer P(MA) causes important changes in the different bands.

Two new bands appear in the methoxy region. The first one is visible as a shoulder at 6.35 τ (band e) in the spectrum of a copolymer containing 4% A units (Fig. 10). Its intensity increases with the percentage of A (Fig. 11). When this percentage reaches 30%, a third band is observed at 6.32 τ (band h in Fig. 12). Correspondingly, band a decreases steadily and vanishes when the percentage of A units is 55% (Figs. 13 and 14). Because the resonance of the

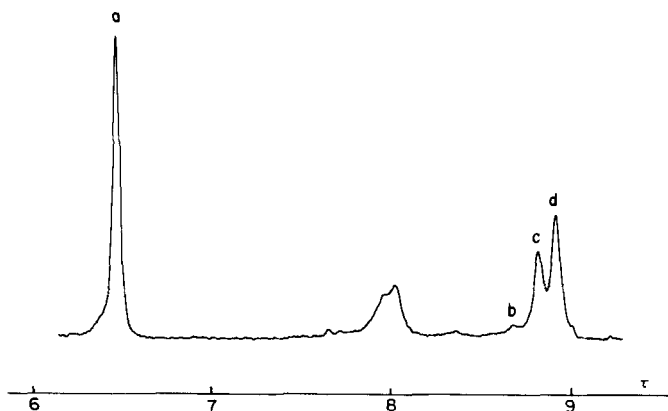


Fig. 9. NMR spectrum of homopoly(methyl methacrylate) in pyridine solvent at 100°C (60 MHz).

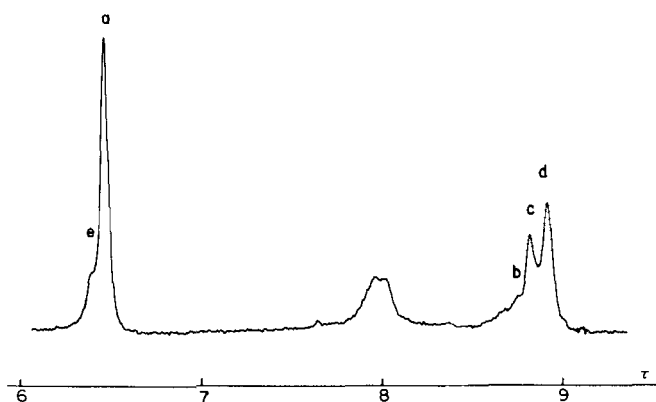


Fig. 10. NMR spectrum of poly(methyl methacrylate-acrylonitrile) with 95% M in pyridine solvent at 100°C (60 MHz).

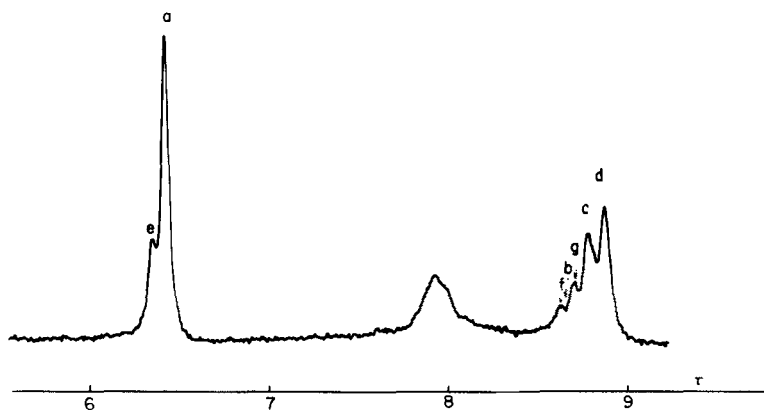


Fig. 11. NMR spectrum of poly(methyl methacrylate-acrylonitrile) with 82% M in pyridine solvent at 100°C (60 MHz).

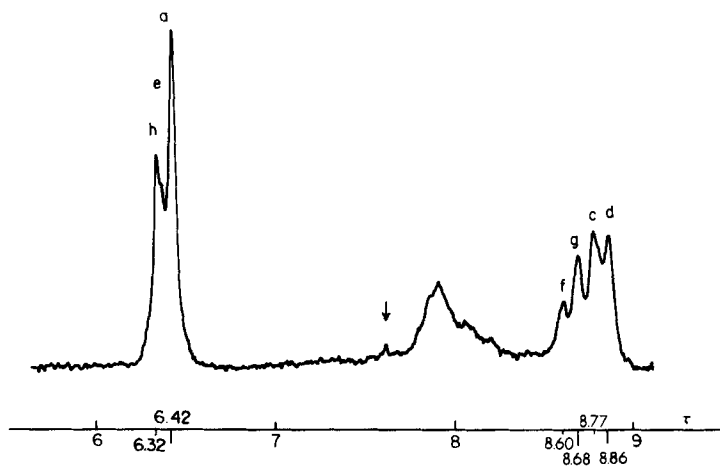


Fig. 12. NMR spectrum of poly(methyl methacrylate-acrylonitrile) with 70% M in pyridine solvent at 100°C (60 MHz) (impurity: ↓ pyridine).

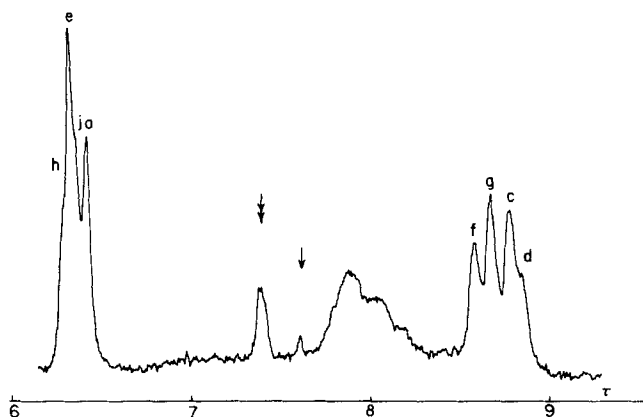


Fig. 13. NMR spectrum of poly(methyl methacrylate-acrylonitrile) with 63% M in pyridine solvent at 100°C (60 MHz) (impurities: ↓ pyridine; ↓ DMF).

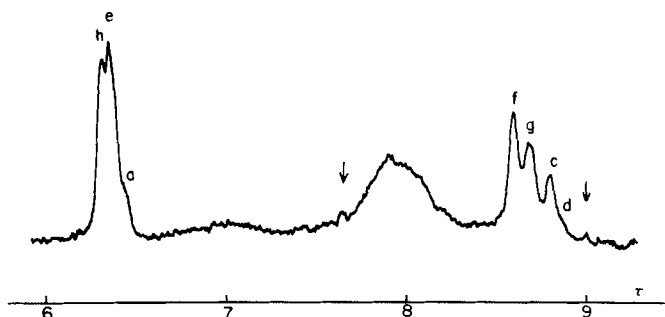


Fig. 14. NMR spectrum of poly(methyl methacrylate-acrylonitrile) with 45% M in pyridine solvent at 100°C (60 MHz) (impurity: ↓ pyridine).

methoxy protons in the poly(methyl methacrylate) is a singlet independent of the tacticity, the new bands may be attributed to two kinds of M units adjacent to A units and the paramagnetic influence of the nitrile group of A causes the shift of the resonance to lower values of the magnetic field.

Concerning the α -methyl protons, two new bands at 8.62 τ (f) and 8.71 τ (g) appear in the spectrum shown in the Fig. 11. It may be seen that the intensity of f increases steadily with A content, but the intensity of g passes through a maximum. The intensities of c and d decreases gradually (Figs. 11-14). The band d vanishes like a for the copolymer with 55% A (Fig. 14).

No spectrum shows traces of two symmetrical doublets (AB type) centered at about 7.6 τ and 8.3 τ , which could be associated with β -CH₂ protons of MM isotactic diads [9], so that neither f nor g can be attributed to α -CH₃ protons in isotactic triads.

When the A content is very high (80%), only the f band is important in the α -CH₃ region, as shown in Fig. 15. In this case most of the M units are isolated between two A units, and we suggest that f' is to be attributed to the α -CH₃ protons of such isolated M units. The slight difference between the position of the f and f' bands is due to the difference in solvent mediums.

In this case also, h' is more important in the methoxy region and corresponds probably to isolated M units adjacent to two A units, while the e (and e') band corresponds to M units adjacent to only one A unit.

The poor resolution of the spectra of the β -CH₂ groups of M and A units and of the α -CH groups of the A units does not allow interpretation. In particular, the α -CH absorption is broadened between 6.2 τ and 7.6 τ and overlaps the methoxy proton region. Such a broadening is probably caused by the poor solubility of the

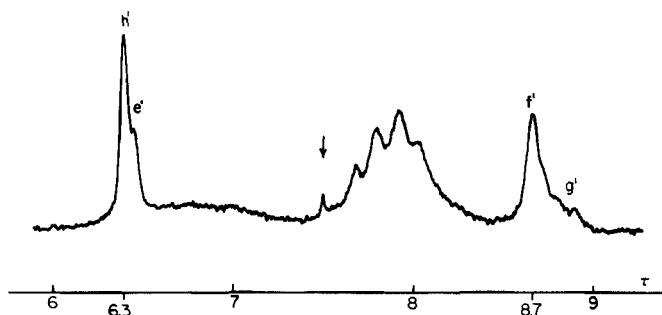


Fig. 15. NMR spectrum of poly(methyl methacrylate-acrylonitrile) with 20% M in pyridinium-chloride solvent at 90°C (60 MHz) (impurity: ↓ pyridine).

copolymers. The homopolymer of A is not soluble in the solvents used and the upper limit of solubility in pyridium is reached when the A content is 68%; then the number-average length of the sequences of A units is 2.4, and for longer sequences the M units cannot maintain the copolymer in solution.

NMR QUANTITATIVE STUDIES

These studies have dealt with the composition of the copolymers, the determination of the number-average length of M sequences, and the analysis of the short sequences. They were carried out by graphical resolution of the multiplets and planimetry.

The mole per cent of M in the copolymers is obtained using the intensity X of the methoxy group, the total intensity Y of the α -CH₃, β -CH₂, and α -CH groups, and the intensity Z of the α -CH₃ groups. The expression is

$$M\% = \frac{X}{X + Y - 2X/3} = \frac{Z}{Z + Y - 2Z/3} \quad (4)$$

The second member of Eq. (4) is used when the copolymer is rich in M units, and the third member when the copolymer is rich in A units, because in this last case the measurement of X is perturbed by the α -CH groups of the A units, as shown in the Fig. 15. Fig. 16 shows the results plotted versus the composition of the monomer feed and then compared with the experimental results deduced from chromatographic analysis of the copolymerization medium; the calculated curve takes into account the penultimate effects. The agree-

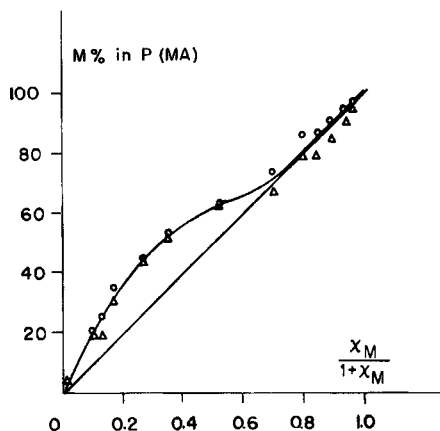


Fig. 16. Calculated composition curve and experimental points.
 Δ , NMR data; \circ , gas chromatography data.

ment is rather good and it also may be seen that when the M contents of the feed is greater than 60%, copolymerization is practically azeotropic.

The following method, based on the analysis of the OCH_3 bands, for the determination of the number-average length of M sequences, say $\overline{L_M n}$, was used. Band a is attributed to the $(n - 2)$ inner units of the M sequences of average lengths n , and the bands e and h correspond to the two terminal units of these sequences. Then the ratio of their intensities is

$$I(a)/I(e + h) = (n - 2)/2 \quad (5)$$

and then

$$\overline{L_M n} = n = 2[1 + I(a)/I(e + h)] \quad (6)$$

This method assumes, of course, that the number of isolated M units is negligible and is valid only when X_M is great enough. However, if X_M is low, the two calculated values of $\overline{L_M n}$ [Eqs. (1) and (1')] are close, as the results plotted in Fig. 17 show and the NMR data do not allow us to make a choice between them. However, for the large values of X_M , the NMR data support the presence of the penultimate effects, and again seem to indicate a more pronounced effect.

From the composition of the copolymer and the value of $I(e + h)$, it is possible also to deduce the run number, such as defined by Harwood and Ritchey [11], and then to determine $\overline{L_M n}$ by another

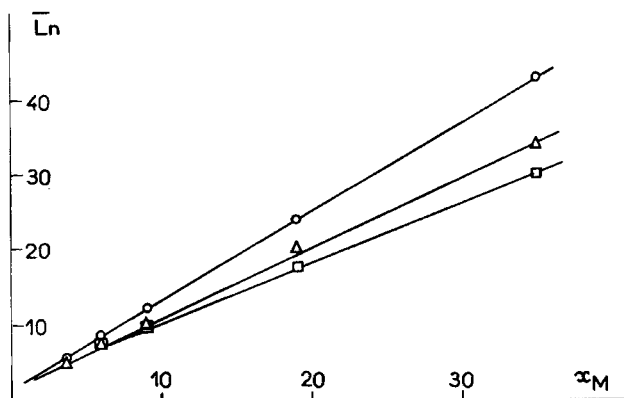


Fig. 17. \bar{L}_n , \bar{L}'_n , and $(\bar{L}_n)_{NMR}$ versus x_M . O, without penultimate effects; Δ , with penultimate effects; \square , $(\bar{L}_n)_{NMR}$.

method. Using the composition data given by the chromatographic measurements [1] one obtains identical results.

Quantitative data about the analysis of the short sequences may be obtained from examination of the α -CH₃ bands. In pure poly-(methyl methacrylate) these bands are sensitive to the tacticity of the triads of the sample, so that in the copolymers it would be necessary to consider the possibility of the cotacticity, as suggested by Bovey [12]. The meaning of this concept and the notations which would be necessary are illustrated in Table 1 for the sequences containing isolated M units. However, as shown in Fig. 15, the f band attributed to these isolated M units is not resolved enough. NMR analysis at 100 MHz does not improve the resolution. Then we may assume that the resolution of the triads is limited to the inner units of the M sequences.

Considering all the spectra obtained, we suggest the following interpretation for α -CH₃ spectra:

1. Band f, as already indicated, is attributed to the isolated M units, or M_1 sequences.

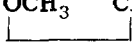
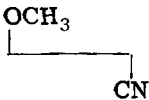
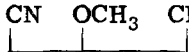
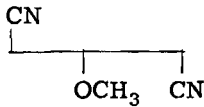
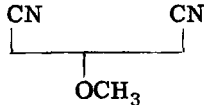
2. Band g is attributed to the two M units of the M_2 sequences. A very small part of the band may be due to the isotactic triads of the long M sequences.

3. Band c is the sum of two parts: the heterotactic triads of the long M sequences and the two terminal units of the M_x sequences, with $x \geq 3$.

4. Band d, of course, is caused by the syndiotactic triads of the long M sequences.

A few experimental results concerning the M_1 and M_2 sequences of copolymers rich in A units are plotted in Figs. 4 and 5 and it may

Table 1. Nomenclature for Diads and Triads in Cotactic Isolated M Units

Diads	OCH ₃ CN	
Coisotactic		I'
Cosyndiotactic		S'
Triads	CN OCH ₃ CN	
Coisotactic		i'' = I' I'
Coheterotactic		h'' = S' I'
Cosyndiotactic		s'' = S' S'

be seen that, although the experimental error may be rather large, the best fit is obtained with calculated curves which take into account the penultimate effects.

The calculated value, in the penultimate-effect case, of the sum S_T of the terminal units of the M_x sequences ($x - 3$) is as follows:

$$S_T = 2 \frac{P_{MMA} \cdot P_{AMM}}{P_{MMA} + P_{AMM}} \left(\frac{1}{1 - P_{MMM}} - 1 \right) \quad (7)$$

But it is not possible to check the intensity of the c band according to Eq. (7) because the contribution of the heterotactic triads of long M sequences is unknown: One may suppose that it obeys the probability P_h according to Bovey's $\sigma(0, 24)$, but it is not certain that this value should be valid for the rather short M sequences present in the copolymer. Also, such evaluation is based on Bernoullian statistics, which have been proved in this paper to be incorrect. However, calculated values of S_T are given in Table 2.

The resolution of the methoxy protons of the terminal M units is rather poor and only the isolated M units give a distinct h band corresponding to the f band of the CH₃ protons. In a few cases, however, it is possible to observe a shoulder j on the e band (Fig. 13). Tenta-

Table 2. Calculated Amount of Terminal Units of M_x Sequences ($x-3$) for Different Values of Copolymer Composition x_M

Fig No.	12	13	14
x_M	2.38	1.12	0.37
S_T , ^a %	30	28	12

^aIn per cent of M units.

tively we may suggest that this shoulder corresponds to the terminal units of the longer M sequences.

CONCLUSION

Through the study of the sequence distribution, analysis of the IR and NMR spectra of the copolymers acrylonitrile-methyl methacrylate gives support to the proposal that penultimate effects exist. These effects have been previously proposed to account for the peculiar kinetic behavior observed when the feed was poor in acrylonitrile. This statement is based on the study of short sequences containing one or two M units. It suggests that Bernoullian statistics do not apply correctly. But it is not possible to precisely state the order of the Markovian statistics, which would be convenient. Conversely, the occurrence of penultimate effects allows us to make a correct interpretation of some features of the NMR spectra of copolymers.

REFERENCES

- [1] A. Guyot and J. Guillet, *J. Macromol. Sci.*, **A2**, 887 (1968).
- [2] A. Guyot and J. Guillet, *J. Macromol. Sci.*, **A1**, 793 (1967).
- [3] W. G. Barb, *J. Polymer Sci.*, **11**, 117 (1953).
- [4] E. Mertz, T. Alfrey, and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).
- [5] G. E. Ham, *Copolymerization*, Wiley-Interscience, New York, 1964, p. 16.
- [6] M. Berger and I. Kuntz, *J. Polymer Sci.*, **A2**, 1687 (1964).
- [7] R. Schmolke, H. Herma, and V. Gröbe, *Faserforsch. Textiltech.*, **16**, 589 (1965).
- [8] Pham Quang Tho, J. Guillet, and A. Guyot, *Compt. Rend.*, **264**, 2019 (1967).
- [9] F. A. Bovey, *Pure Appl. Chem.*, **12**, 525 (1966).

- [10] R. M. Miller and L. E. Nielsen, *J. Polymer Sci.*, **46**, 303 (1960).
- [11] H. J. Harwood and W. M. Ritchey, *J. Polymer Sci.*, **B2**, 601 (1964).
- [12] F. A. Bovey, *J. Polymer Sci.*, **62**, 197 (1962).

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